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(54) Seal

(57) A seal, especially a cylinder head gasket, is provided with a sealing body produced by rolling of expanded graphite particles and containing furan resin at least over part of its thickness. An excessive bonding of the seal to the opposing surfaces is prevented by the resin content.

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SPECIFICATION
Seal

This invention relates to a sealing body, especially a cylinder head gasket, produced by compressing expanded graphite particles using rollers.

Powdered and particulate graphite, especially natural graphite, has been used in admixture with ceramic and metallic materials and with synthetic resins for a long time in the manufacture of seals and packings of all types (see for example, Chem.-Ing.-Technik 22, 1950, 284). It is desirable to take advantage to as great an extent as possible of the suitable material properties of graphite when making seals and packings which are to be exposed especially to high temperatures or aggressive media, that is to say, the extent of their use in seals and packings should not be limited by the addition of other materials.

Various natural types of graphite, especially flake-formed natural graphites, are comparatively plastic and may be pressed to form bodies of different shape, for example to plates or rings, without additions of binders or of materials otherwise promoting bond strength. Their use, especially in the manufacture of seals is generally not possible at all or is possible only to a limited extent on account of their low strength. Moulded graphite articles with an essentially larger strength may be obtained when using a process disclosed in German Auslegesschrift 12 53 130, in which graphite particles are treated with one or several oxidising acids to form a graphite intercalation compound which is then decomposed by the action of heat. In this way there are produced concertina shaped inflated or expanded graphite particles which can be compressed for example by rollers or die presses to flexible foils or layer bodies which consist exclusively of graphite.

Bodies produced from expanded graphite particles are advantageously used as seals, packings, brushes, radiation shields and the like and there has been no lack of experiments to make use of the suitable temperature and corrosion resistance of this physiologically unobjectionable material particularly in the manufacture of flat seals, especially for cylinder head gaskets. These gaskets consist essentially of a core made of sheet metal, metal gauze or some alternative reinforcing insert which inserts are in alignment with bores in the cylinder head and graphite layers produced by compression of expanded graphite particles to cover the surface of the core. A flat seal with a metal supporting core on which graphite layers are rolled on both sides is known for example from German Utility Model 75 26 276. In a gasket disclosed in German Offenlegungsschrift 24 04 544, the graphite layers consist of zones f different density and thickness so that on tightening the seal an additional sealing effect is achieved.

Flat seals are clamped in use between opposing surfaces, as a result of which larger compressive stresses exist in the seals. As a result of a large number of dislocation and displacement processes in which the graphite crystals forming the graphite layers are displaced with respect to one another, the graphite flows or creeps into all the depressions of the opposite surface and completely matches the contours of this surface. In this process which is advantageous from the viewpoint of the sealing effect produced, the adherence between the graphite layer and the opposite surface increases greatly so that the graphite can often only be detached from the opposite surface by destruction of the seal. It is also necessary, to apply larger forces for effecting separation, for example of the cylinder head from the cylinder.

It is known to cover the surface of the seals with a material which reduces static friction (German Offenlegungsshrift 24 41 602). Suitable substances according to these proposals are compounds with a layer lattice structure such as molybdenum sulphide, boron nitride and graphite fluoride, temperature resistant antiadhesive polymers, such as polytetrafluoroethylene and polyamide, and metal soaps. In addition, the layers can also contain abrasive substances such as silica flour. These seals do not however always lead to the required result of achieving the reliable removal of the covering or coating from the seal. It is finally also known to provide seals made from a soft material with thin surface layers which contain graphite, talc and similar substances in order to overcome the adhesion of the seal on the opposite surfaces (see German Patent Specification 1,264,902). In particular, talc-containing layers prevent the adhesion of seals under certain conditions. In some fields, for example with cylinder head gaskets, the adhesion of the seal cannot however be avoided, rather the talc leads to a more frequent sticking between seal and opposite surface.

According to the present invention, there is provided a sealing body produced by rolling of expanded graphite particles which contains a cured furan resin as defined herein extending through at least part of its thickness.

According to a preferred embodiment of the invention, the sealing body only contains furan resin over a part of its thickness, the thickness of the furan resin-containing part of the sealing body amounting preferably to 0.05 to 0.15 mm. The sealing body is preferably a cylinder head gasket formed from a plurality of layers of compressed expanded graphite particles, which comprises several openings intended to be aligned with the cylinder bores and any other recesses present in an engine.

By the term furan resin as used herein is meant a thermoplastic resin formed by condensation of furfuryl alcohol or furfurol. The furan resin content of the sealing body gives rise to a stiffening of the graphite particles inhibiting the flowing or creeping of the graphite particles so that depressions in the surface opposite to the sealing body are not filled out with graphite. The bond strengths between seal and opposite surface are

lower so that the parts do not bond with one another and may easily be detached from one an ther. It is not necessary to add furan resin to the sealing body over its entire thickness for this surprising effect to be achieved. Rather it is sufficient for a comparatively thin zone to extend from the surface of the seal. The thickness of this zone is so measured that the flowing or creeping of graphite in the region of the sealing body facing the opposite surface is suppressed and the flexibility of the overall body is essentially obtained and is not influenced beyond the amount absolutely necessary. The most suitable thickness for the furan resin depends correspondingly also on the thickness of the seal, with in general thin layer seals also requiring thinner zones filled with resin.

Seals and packings formed of graphite which are produced by moulding expanded graphite particles together with a phenolic condensation product are known from United States Patent Specification 1,137,373. Such seals and packing possess an especially high strength which cannot be achieved with conventional non-expanded natural graphite particles. On the other hand the bodies are not flexible so that flat seals produced therefrom break easily and often no sealing effect is achieved.

In producing seals embodying this invention, furfuryl alcohol or furfurol and a hardening catalyst dissolved therein are applied for example by spraying or brushing to the upper surface of the sealing body for the production of the body according to the invention. The solution is soaked up into the body by capillary forces, with the rate of penetration being very small on account of the small capillary diameter. It is indeed known to impregnate porous carbon and graphite bodies with furan derivatives, especially with precondensates which possess an essentially greater viscosity than the monomers. When impregnating porous carbon and graphite shaped articles with furfuryl alcohol directly, it is necessary to provide the bodies to be impregnated with special covering layers in order to reduce loss of the impregnating material and to achieve a definite degree of filling. According to German Patent Specification 16 71 006, there is used for this purpose an air drying covering layer formed of polyvinylacetate. These procedures do not need to be used when carrying out the present invention, particularly on account of the characteristic pore structure and pore size distribution of the graphite bodies produced by compression of expanded graphite particles. Precondensates based on furan derivatives or phenol compounds moreover do not diffuse under high pressures — presumably on account of their molecular size — into the sealing body, but surprisingly monomeric furfuryl alcohol and furfurol do. These compounds penetrate with a small, essentially uniform speed into sealing bodies formed of compressed expanded graphite particles even without the use of pressure and remain in the bodies during heat treatment necessary for the condensati n and hardening of the resin, so that only very small losses arise. The thickness of the zone of a sealing body filled with furan resin can therefore be determined fr m the penetration time with sufficient precision on account of the essentially uniform penetration rate of the monomers, and can be set in advance.

Weak acids and acid anhydrides, for example maleic anhydride, benzene sulphonic acid, etc., whose concentration in the impregnating material should amount appropriately to about 5 to 15%, are especially suitable as condensation agents and hardening catalysts for the monomers, especially furfuryl alcohol. A 90% furfuryl alcohol and 10% maleic anhydride-containing solution, which is sprayed or brushed on to the sealing body is particularly preferred. After impregnating, the residue of the solution has to be removed from the surface of the sealing body e.g. after a penetration time of 5 to 10 minutes in accordance with the desired depth of penetration. Since residues remaining on the surface form a sticky resin in the condensation treatment, care should be taken to obtain a complete removal of the solution, for example with a rubber blade, a sponge or an absorptive cloth.

The impregnated or partially impregnated sealing body is then heated in a first step to 80 to 140°C and after a period of about one hour in a second step to 180 to 220°C and the temperature is likewise held for about one hour. Impregnation and heat treatment are carried out suitably in this way with seals which contain metal or other cores. According to another procedure, the sealing body is firstly impregnated on one side, the impregnating material is hardened and the body is then pressed or rolled onto the core. If necessary the shaping conditions must be matched to the somewhat greater stiffness of the pre-impregnated sealing body.

The following examples illustrate this invention.

EXAMPLE 1

Expanded graphite particles formed by thermal decomposition of graphite hydrogen sulphate were rolled to a foil-type layer body with a thickness of 2 mm whose bulk density amounted to about 1.0 g/cm³. The laminated body was divided up and one part was coated with a solution containing 90% by weight furfuryl alcohol and 10% by weight maleic anhydride, another remaining unimpregnated. After a duration of 10 minutes, residual solution was wiped off from the treated body, the weight increase of the body amounting to about 2%, corresponding to 40 g/m². The impregnated body was heated to 120°C and then 200°C, the residence times at these temperature steps being respectively one hour. Both the treated and the untreated bodies (100 x 50 x 2 mm) were clamped between polished steel plates (Material — No. 1.1203), the surface pressure amounting to 50 N/mm². After a test time at room temperature of seven days, both sealing bodies could be easily separated from the opposite surfaces.

EXAMPLE 2

The testing step of Example 1 was repeated at a temperature of 200°C and under the same pressure on graphite bodies, both impregnated and unimpregnated produced by the procedures of Example 1. The untreated laminated body adhered very firmly to the steel plates and could not be separated from the steel plates without being destroyed. The laminated body which had been treated with the furfuryl alcohol solution did not stick to the steel plates and could be removed easily therefrom.

CLAIMS

1. A sealing body produced by rolling of expanded graphite particles which contains therein a cured furan resin as defined herein.

2. A sealing body according to claim 1, in which the furan resin extends over a part of its thickness only.

3. A sealing body according to claim 1 or 2, wherein the furan resin is present to a depth of from 0.05 to 0.15 mm.

4. A sealing body according to claim 1, 2 or 3, which is a cylinder head gasket formed from a plurality of layers of compressed expanded graphite particles, which comprises several openings intended to be aligned with the cylinder bores and any other recesses present in an engine.

5. A sealing body, substantially as described in the foregoing Example 1.

6. A process for the production of a sealing body which comprises covering a flat body formed by rolling of expanded graphite particles with a solution of a furan derivative selected from furfuryl alcohol and furfurol and a hardener catalyst, removing the flat body from contact with excess solution after a period of 5 to 10 minutes and heating the flat body for condensation and hardening of the furan resin in a first step to 80 to 140°C and in a second step to 180 to 220°C.

7. A process according to claim 6, wherein the solution is applied only to a part of the surface of the flat body.

8. A process as claimed in claim 6 or 7, wherein the solution is applied to the flat body in sufficient quantity for a furan-containing layer of 0.05 to 0.15 mm thickness to be produced.

9. A process as claimed in any one of claims 6 to 8, wherein the hardener is benzene sulphonic acid or maleic anhydride.

10. A process as claimed in any one of claims 6 to 9, wherein the concentration of the hardener in said solution is from 5 to 15% by weight.

11. A process according to any one of claims 6 to 10 wherein the flat body is covered with a solution of furfuryl alcohol and maleic acid anhydride in a 90:10 weight ratio.

12. A process for the production of a sealing body, substantially as described in the foregoing Example 1.

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